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## OCCURANCE, PREDICTION AND PREVENTION OF ZINC SULFIDE SCALE WITHIN GULF COAST AND NORTH SEA HIGH TEMPERATURE/HIGH SALINITY PRODUCTION WELLS

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### Abstract

Precipitation of mineral scales causes many problems in oil and gas production operations: formation damage, production losses, increased workovers in both producers and injectors, poor injection water quality, and equipment failures due to under-deposit corrosion. The most common mineral scales are sulfate and carbonate-based minerals. However, scale problems are not limited to these minerals and there have recently been reports of unusual scale types such as zinc and lead sulfide. This paper focuses on zinc sulfide scale that has been found in several fields along the Gulf Coast of the USA and fields within the North Sea Basin. Scale deposition has caused significant pressure and rates reductions in high temperature, high rate gas, condensate and black oil wells. After acid washes to remove zinc sulfide scale (and other acid soluble solids), production rates and flowing tubing pressures returned to previous levels, but new scale deposits formed in many wells and re-treatments were required. Topside process equipment most noticeable low-pressure separators and hydrocyclone were observed to suffer reductions in performance owing to zinc sulfide scale deposition. In addition, there are significant risks associated with acid treatments in high temperature, high-pressure gas wells: corrosivity of the acid at high temperatures (general corrosion, sulfide stress cracking, and chloride stress cracking) and safety (hydrogen sulfide generation by acid dissolution of zinc sulfide plus high pressure pumping). One possible method for preventing production declines and reducing the need for high temperature, high-pressure acid jobs, is to use scale inhibitors or a chelating agents to prevent the formation of zinc sulfide scale. The relative effectiveness of eight scale inhibitor chemistries and two chelating agents in preventing formation of zinc sulfide scale has been determined. The

required scale inhibitor concentrations are significantly higher than concentrations needed for common sulfate and carbonate scales. For chelating agents, it is possible to prevent the formation of zinc sulfide scale with the required concentrations being proportional to the  $Zn^{2+}$  ion concentration in the scaling brine. This paper outlines the testing methods utilized for chemical screening and for prediction so that assessment of the potential problem within fields during appraisal can be assessed prior to production commencing and a method of managing the risk made available.

### Introduction

The most common scales encountered in oil field operations are sulfates such as calcium sulfate (anhydrite, gypsum) barium sulfate (barite), strontium sulfate (celestite) and carbonates (calcite). Numerous studies on scale inhibition have been published over the past few years with regard to controlling such scale within the reservoir and in production equipment (downhole and topside).<sup>1-8</sup> Other less common scales have also been reported such as iron oxides, iron sulfides and iron carbonate. These scale types are most commonly associated with iron generation from corrosion products although iron carbonate scale has been reported forming from produced water drawn from formations where iron containing authigenic minerals are present within the formation.<sup>9,10,11</sup> As with the sulfate and carbonate scale types described above even iron carbonate scale is able to be controlled by inhibitor molecules.<sup>12</sup>

Lead and zinc sulfide scale has recently become a concern in a number of North Sea oil and gas fields. These deposits have occurred within the production tubing and within the topside process facilities. Investigation of the literature lead to a number of references where such scale had been observed<sup>13,14,15,16,17</sup> but very little information was available on their inhibition by chemical means. A recent review paper outlines formation mechanisms of both lead & zinc sulfides and also reviews the data from the literature before describing how a chemical inhibition program has been effectively deployed within a North Sea field<sup>18</sup>.

**Potential sources of Lead and Zinc sulfide.** Several sources of zinc/lead ions and sulfide ions are possible within produced fluids.

**Potential sources of zinc and lead ions include**

- Reaction products of formation minerals (sphalerite Zinc sulfide and Galena PbS) during connate and aquifer water contact over many millions of years could result in partial mineral dissolution.<sup>13,14,15</sup> Zinc ion concentration within high pressure/temperature fields within the Gulf coast of Mexico<sup>16</sup> were reported as high as 70 ppm Pb and 245 ppm Zn.
- Reaction of injected water used for pressure support into the aquifer or oil leg can result in the fresh or seawater reacting with minerals within the formation can become enriched in heavy metal ions.
- Zinc ions sourced from heavy brine completion fluids lost into the formation during drilling and well workover operations (Zinc bromide). Biggs<sup>17</sup> reported that a loss of 500 bbls of 17.2 ppg zinc bromide completion fluid within a reservoir resulted in significant zinc sulfide scale formation with the presence of 2 ppm of hydrogen sulfide from the reservoir. In an oil field operated in the North Sea UK sector the presence of zinc sulfide on downhole gauges and logging tools was reported within a well where zinc bromide brines had been lost during completion operations. Zinc levels within the produced fluids were in the region of 10 to 50 ppm for several months during initial water breakthrough.

**Potential sources of sulfide ions include:**

- Hydrogen sulfide gas. Hydrogen sulfide gas is the most likely source of sulfide ions to allow the formation of lead/zinc sulfide scale. Low concentration in the tens of ppm levels of H<sub>2</sub>S have been reported in produced gas from wells where lead and zinc sulfide scale problems have been reported.
- Decomposition of drilling compounds and corrosion inhibitor within heavy brines. The decomposition of corrosion inhibitor and drilling compounds can also produce sulfide ions at high temperature when tested in autoclave equipment but are very unlikely to be the source of sufficient sulfide ions to give scale deposition over many years of production. The most likely source of sulfide ions is from reservoir hydrogen sulfide gas.

**Zinc and Lead sulfide solubility.** Lead and zinc sulfide solubility data in a 1M NaCl brine solution are presented in Figure 1. Also given on this figure is the solubility of iron sulfide for comparison. It is generally believed that iron sulfide is very insoluble and hence is a common oilfield scale. However from the data presented in Figure 1, it is clear that both lead and zinc sulfides have much lower solubility. At pH 5 the solubility of iron sulfide is 65 ppm whereas lead and zinc sulfides are 0.002 ppm and 0.063 ppm respectively. Depending on the exact brine conditions, the solubility of zinc sulfide is between 30 and 100 times more soluble than lead sulfide. As with iron sulfide, the solubility of both lead and zinc sulfide increases with increasing solution pH. This is the

principle reason why simple acid washing of sulfide scales is so effective at removing these deposits. Solubility data presented by Barrett and Anderson<sup>19</sup> suggest that the solubility of lead and zinc sulfide increases with increasing temperature and increases with increasing brine salinity. These data are shown in Figures 2 and 3. From this data it is clear that if during the production of high temperature brines, these brines are cooled within a production system, the formation of zinc and lead sulfide scales could arise. The dilution of a high salinity brine and the increased solution pH caused by injection water mixing with the formation brine could also result in sulfide scale formation, with the preferential formation of lead sulfide over zinc sulfide if the ions were present in the brine in equal amounts.

The very low solubility of lead and zinc sulfide would make it unlikely that zinc/lead and sulfide ions could exist together in solution for any length of time. It is more likely that the zinc/lead ion source mixes with the hydrogen sulfide rich source within the near-wellbore or production tubing during fluid extraction and from then on the changes in temperature, solution pH and residence time control the location within the process system where the scales deposit. From the literature, it is known that within a single reservoir interval two brine types can co-exist.<sup>20</sup> For example, connate water can have a different composition to aquifer water, and both can exist separately whilst being in thermodynamic equilibrium until mixed within the near-wellbore and production system. In addition, aquifer water/connate water can be separated from the dissolved hydrogen sulfide gas within crude oil or gas cap until production brings these sources together.

**Chemical and Mechanical Removal**

Mechanical removal of scale deposits is not an uncommon procedure from easily assessable process equipment but does rely on the ability to gain access to the affected components and is normally associated with disruption to oil/gas processing. Mechanical means such as jetting of pipe work and valves is an effective way of removing deposits in the short-term but often needs to be repeated (at intervals from 4 weeks to 6 months). Deferred oil costs and equipment rental costs can be very high if mechanical removal is required within the production string, and, moreover, milling might be required to remove significant restrictions.

Chemical removal such as acid washes (hydrochloric acid normally at concentrations of 15% to 30% v/v) will normally recover the production rate but like mechanical removal new scale deposited will form within the same time period as prior to the chemical removal program.<sup>17</sup> In addition, there are significant risks associated with acid treatments, especially in high temperature and high-pressure wells. Corrosivity of the acid at high temperatures can result in general corrosion in addition to hydrogen and chloride stress cracking. There is also a significant safety implication owing to the generation of hydrogen sulfide gas and applying acids in high-pressure

environments. If iron sulfide is also present within the scale that is being dissolved, it is quite possible that the iron sulfide will be preferentially dissolved relative to the zinc/lead sulfide owing to the significant difference in this compounds solubility. A risk also exists that if the volumes of acid used for the dissolution process are insufficient to completely dissolve the sulfide scales, elemental sulphur could form as a byproduct as the pH rises within the spent acid solution. Test work on alternative acid types, including mixed organic acid formulations, have shown reduced corrosion and hydrogen cracking effects, but their rates of reaction against sulfide scale are much less rapid, and, as a result, the contact time required would be longer. These data are shown in Figure 4. In Figure 4, the rates of dissolution of zinc sulfide at 20°C in the presence of hydrochloric acid, mixed organic acid (formic and acetic) and low molecular weight polymeric acid are presented. It is clear that for low temperatures (offline topside process equipment conditions), acid washing with hydrochloric acid is the most effective method of chemical removal.

### Chemical Inhibition

There is a very extensive literature on the prevention of scale formation using inhibitor chemicals. However, most of this literature is focused on the prevention of sulfate and carbonate scales<sup>1-8</sup> with little having been published on the inhibition of lead and zinc sulfide scales. Scale inhibitors function at substoichiometric concentrations with respect to the scaling compound by a number of mechanisms, such as preventing scale nuclei formation, adsorption onto scale nuclei once formed, inhibition of further crystal growth and dispersing growing scale nuclei to reduce solid adherence. Chelating agents, whilst not generally used for conventional sulfate/carbonate scale inhibition, work by forming a stable water-soluble complex with metal ions in solution thus effectively preventing reactions with other ions within the brine.

Laboratory testing of scale inhibitors for application is the most common way of product selection when controlling sulfate and carbonate scale deposition. The issue of handling hydrogen sulfide gas makes such testing for zinc sulfide more difficult. Kaplan<sup>21</sup> describes a laboratory method of screening products and the effectiveness of these products is substantiated with field test data. Emmons and Chestnut<sup>22</sup> also outline field test data that shows that zinc sulfide scale control was possible by application of polymer based scale inhibitors.

### Experimental Evaluation of Zinc sulfide inhibitors and chelants

**Scale Inhibitors and Chelating Agents.** In a recent study, several scale inhibitor chemistries, which could prevent sulfate and carbonate scale, were short-listed for assessment for their control of zinc sulfide. In addition, the ability of two commercial chelating agents to prevent zinc sulfide

precipitation was determined. A list of scale inhibitor and chelating agent abbreviations or product names, generic types, compositions, and molecular weights are given in Table 1. Generic types of scale inhibitors tested were phosphate ester, phosphonates, and polymers. Polyaminocarboxylic acid chelating agents were tested. The scale inhibitors tested are active ingredients in currently available scale inhibitors. The purpose of this study was to identify scale inhibitors or chelating agents, which could prevent precipitation of Zinc sulfide scale.

**Test Procedure** A laboratory test procedure similar to the standard static bottle test procedure originally developed for the evaluation of sulfate scale inhibitors was designed for evaluation of zinc sulfide scale inhibitors or chelating agents<sup>7</sup>. These tests are comparative performance tests, and like the sulfate bottle test, measure the amount of scaling ions that remain in solution relative to a blank and the base brine composition. This allows the percent inhibition to be determined as a function of inhibitor or chelant concentration.

In the zinc sulfide tests, various concentrations of scale inhibitor or chelating agent are added to brine solutions capable of precipitating a known amount of zinc sulfide scale when heated to 165°F. Tests were conducted at a zinc sulfide loading of 37 mg/litre except for two series in which the zinc sulfide loading was increased to 75 and 150 mg/litre respectively. All tests were conducted in 5% NaCl brine at 165°F. Differences in amounts of zinc sulfide scale formed with and without scale inhibitor or chelating agent are measures of scale inhibitor/chelating agent effectiveness. Amounts of scale formed were determined by analysing the test brines for  $Zn^{2+}$  ion concentrations. Test results are reported as percent inhibition or percent chelation as a function of scale inhibitor or chelating agent concentration used in the test

### Discussion

The relative effectiveness of eight scale inhibitors and two chelating agents (Table 1) in preventing formation of zinc sulfide scale in 5% NaCl brine containing 37 mg/litre zinc sulfide was determined at scale inhibitor concentrations from 10 to 100 mg/litre. For the chelating agents, molar ratios of chelating agent to zinc sulfide ranged from 1:1 to 4:1. Test results are summarized in Figures 5, 6 and 7 for the scale inhibitors and in Figure 6 for the chelating agents. The effect of zinc sulfide loading, i.e., the level of supersaturation or saturation ratio, SR, on the performance of one scale inhibitor is shown in Figure 8 (zinc sulfide loading ranged from 37 to 150 mg/litre).

Scale inhibitor performance varies between generic types of scale inhibitors as well as within each generic type. The effectiveness of the scale inhibitors could be due to one or more of the following factors: threshold scale inhibition at substoichiometric concentrations, and/or the low brine pH

arising from the acidity of the scale inhibitor or by ion chelation. The required scale inhibitor concentrations are significantly higher than concentrations required for common sulfate and carbonate scales. Different saturation ratios for specific field applications will also affect required scale inhibitor concentrations (see the Scale Inhibitor/Chelating Agent Selection section).

**Phosphate Ester Scale inhibitor** Results of zinc sulfide scale inhibition tests using a phosphate ester (triethanolamine phosphate ester, TEAPE) inhibitor are shown in Figure 5. These data show that TEAPE is not effective against zinc sulfide. Molar ratios of  $Zn^{2+}$ /TEAPE ranged from 11:1 at 10 mg/litre TEAPE to 1:1 at 100 mg/litre TEAPE.

**Phosphonate/Phosphonic Acid Scale Inhibitors** Results of zinc sulfide scale inhibition tests using three phosphonate scale inhibitors are shown in Figure 6. DTPMP< HEDP< and ATMP are three different phosphonates which are the active ingredients in many commercial products. Although each of the three phosphonates contains similar functional groups (one or more phosphonic acid groups), the overall molecular structures are different. The phosphonate-type scale inhibitors are available in acid (phosphonic acid) or salt (phosphonate) forms. Most phosphonate scale inhibitors are also good chelating agents.

The data shown in Figure 6 suggest that DTPMP, HEDP and ATMP are effective at concentrations from ranging from 50 to 100 mg/litre

The effectiveness of is due to threshold scale inhibition and/or low brine pH. Molar ratios of  $Zn^{2+}$ /scale inhibitor ranged from 17:1 at 10 mg/litre DTPMP to 17:1 at 100 mg/litre DTPMP. This means that DTPMP was effective at substoichiometric concentrations and prevention of Zinc sulfide scale formation was not due to chelation of the dissolved zinc by the scale inhibitor. However, DTPMP is a fairly strong acid and the pH of 10-100 mg/litre solutions of DTPMP in 5% NaCl range from 4.5 to 3.1. Therefore, part of the effectiveness of DTPMP at higher concentrations may be due to a low brine pH. The effect of pH is probably relatively small, however, since the solubility of Zinc sulfide in pH 3 brine is only about 4 mg/litre (Figure 1).

The effectiveness of HEDP and ATMP phosphonates at concentrations of 75 mg/litre or greater is probably due to chelation. Molar ratios of  $Zn^{2+}$ /scale inhibitor are equal to, or less than, 1:1 at 75-100 mg/litre. This means that all of the dissolved zinc can be chelated by 75-100 mg/litre concentrations of HEDP and ATMP. Brine pH values ranging from 3.6 to 4.8 could also dissolve small amounts of Zinc sulfide (Figure 1).

**Polymer Inhibitors** The results of zinc sulfide scale inhibition tests using four polymeric scale inhibitors are summarized in

Figure 7. Overall, the polymers provided the best performance of the three types of scale inhibitors tested. Three of the polymeric scale inhibitors (AMPS/AA, PHOS/MA, and PMA/AMPS) were effective at 25 mg/litre whilst the fourth polymer (PAA2), was effective at 50 mg/litre. The effectiveness of the polymers is undoubtably due to threshold scale inhibition. Molar ratios of  $Zn^{2+}$ /scale inhibitor ranged from 3:1 to 118:1 which means the inhibition of the scale was due to threshold scale inhibition at substoichiometric concentrations of scale inhibitor and was not due to chelation of dissolved zinc by the scale inhibitors.

**Effect of Zinc sulfide Loading on Scale Inhibition** The effect of zinc sulfide loading, i.e., level of supersaturation or saturation ratio, SR, on the performance of the polymeric inhibitor PHOS/MA is shown in Figure 8. At concentrations greater than 25 mg/litre, PHOS/MA provides 96-98% inhibition at a zinc sulfide loading of 37 mg/litre. However, when the zinc sulfide loading is increased to 75 and 150 mg/litre, PHOS/MA becomes less effective. At 75 mg Zinc sulfide/litre loading, 50 mg/litre of PHOS/MA is required to provide greater than 90% inhibition. At 150 mg Zinc sulfide/litre loading, PHOS/MA is not effective at concentrations up to 100 mg/litre. These results are consistent with an earlier study<sup>2</sup> which showed that the required scale inhibitor treating concentrations are determined by the level of supersaturation ratio (SR) of the scaling brine, i.e., as the SR increases, the required scale inhibitor concentrations also increase. Since the zinc sulfide loading in field applications will probably differ from those used in the current tests, field specific performance tests should be conducted to determine the required treating concentrations.

**Chelating Agents** Chelating agents form stable, water-soluble complexes with metal ions and effectively prevent reactions with other ions in the brine, i.e., in this case, sulfide ion. Figure 9 shows the effectiveness of two widely used chelating agents in preventing the formation of zinc sulfide scale. Sequestrene 30A (a 39% aqueous solution of the tetra-sodium salt of ethylenediaminetetraacetic acid, Na<sub>4</sub>EDTA) and CHEL DTPA-41 (a 41% aqueous solution of the pentasodium salt of diethylenetriaminopentaacetic acid, Na<sub>5</sub>DTPA) provide 60-70% chelation of  $Zn^{2+}$  at a 1:1 molar ratio of chelant/ $Zn^{2+}$ . At molar ratios of 2:1 or greater, both products chelate essentially 100% of the dissolved  $Zn^{2+}$  ions and prevent formation of zinc sulfide scale.

Since chelation is a stoichiometric reaction between a chelating agent and a metal ion in solution, the amount of chelating agent required to prevent zinc sulfide scale formation will increase in direct proportion to the  $Zn^{2+}$  ion concentration in the scaling brine. In addition, other divalent and trivalent cations present in a field brine may react with the chelating agent required to prevent scale deposition. Use of chelating agents in brines with significant concentrations of divalent cations may not be cost-effective.

**Scale Inhibitor/Chelating Agent Selection** The data contained in this paper illustrates the importance of selecting the appropriate scale inhibitor chemistry for zinc sulfide scale inhibition.

Additional tests recommended for selection of a scale inhibitor for topside or squeeze treatments are scale inhibitor/brine compatibility and thermal/hydrolytic stability. The combination of scale inhibitor performance tests at specific field conditions (minimum inhibitor concentration, MIC), simulated squeeze tests using field cores, plus scale inhibitor/brine compatibility and thermal stability tests can be used to optimise scale inhibitor squeeze treatments.

Investigation into conventional scale inhibitor performance against lead and zinc sulfate by field trialing a range of products revealed that it was possible to control the formation of these scales. It was found that polymer-based scale inhibitors were far more effective than phosphonate based chemicals and that the treat rates were much lower for scale inhibitor than for chelating agents such as EDTA (ethylenediaminetetraacetic acid) and as a result offered a more cost effective treatment mechanism. The following two case studies will illustrate the points made in the laboratory evaluation of products described above.

**Field A within the UK sector of the North Sea.** Field A is a high temperature/high pressure field in the UK sector of the central North Sea. The field consists of High pressure and temperature gas condensate fluids contained within 3 separate Jurassic reservoirs. One of these accumulations is supported by a natural aquifer. The field is produced from 5 wells drilled to a depth of 4,880 meters TVD. Only two of the five wells are expected to produce formation water.

Initial reservoir pressure was 14,000 Psi and the reservoir temperature is 174°C. The wells produce onto a Normally Unattended Installation where flowrates are measured and chemicals are added to aid flow assurance. From here the fluids are transported via a 30 km multi-phase pipeline to a host-processing platform. The majority of scale issues to date have been reported on the host-processing platform. The field has been on production for three years and produces at a rate of 120 MMscf/d of gas and 28,000 bbls of condensate. Maximum water production to date is 4,500 bbls of water.

The host processing facilities include high pressure and low-pressure separators, and hydrocyclone packages together with gas dehydration and compression. No injection water or gas is used to maintain reservoir pressure within the reservoir. As the water cut within the field increased scale predictions indicated that the formation of calcium carbonate would be the most significant problem across the choke (reservoir pressure of 14,500 Psi to 1,500 Psi) followed by barium sulfate as the temperature declined further. The compositions of the produced fluid from this field are presented in Table 2 from

the initial appraisal well and the true composition upon production. These scales were to be controlled by the application of a low molecular weight phosphonate-based scale inhibitor as determined by dynamic tube blocking tests.

There have been several incidences of "Scale" on Field A as follows:-

- 1) A corrosion probe on the production platform pulled for routine inspection was found to have deposits of zinc/lead sulfide with trace barium sulfate (January 1999), Figure 10.
- 2) Both multiphase flow meters on the Pentland wells (P1 and P2) have shown declines in performance. This decline is inferred to be due to barium sulfate scale. The deposited scale interferes with the rate measurement, but the meters can still be used to predict oil and gas rates. (well P2 November 1998 on formation water breakthrough, well P1 October 1999 on formation water breakthrough).
- 3) Produced water level control valves on high pressure (HP) separator downstream of high pressure hydrocyclones showed a restriction owing to zinc/lead sulfide scale. This occurred in October 1999, just after P1 formation water breakthrough. This valve has been cleaned twice since that date. The scale analysis is shown in Table 3.
- 4) Analysis was performed on a solid sample recovered from a routine pig run of the pipeline to the processing platform, November 1999. This deposit was found to be metal debris plus trace amounts of lead/zinc sulfide and barium sulfate scale.
- 5) Hydrocyclone reject valves have shown fouling due to lead and zinc sulfate deposition.
- 6) P1 Choke, from platform, March 2000. Zinc/lead sulfide was recovered from this equipment during an inspection suggesting that while carbonate/sulfate scale was under control sulfide deposition was still occurring.

The majority of the cases of scale formation have been minor and have not significantly impacted offshore operations. The incident of most concern was the level control valve which required process intervention, disrupts oil in water quality, has manpower implications, upsets the level control and requires low specific activity (LSA) scale handling. This type of scale will deposit in other cold areas of the plant as water cut increases resulting in further processing problems. Controlling this deposition is the major challenge for the field at present.

The discoveries of trace amounts of sulfate scale in early 1999 suggested that while no carbonate scale was forming, the sulfate scale had formed in the presence of the scale inhibitor, although application had been intermittent. The scale inhibitor treat rate was increased from 25 ppm to 50 ppm based on water rate and water samples were taken to confirm the true water composition.

Water analysis carried out across the process system showed that the iron levels were much higher than the 18 ppm thought to exist originally, in fact >200 ppm of iron was present and there where higher levels of lead and zinc. These data are shown in Table 3. The concentration of lead and zinc across the process system may in fact have been higher than that suggested by the analysis as th no appropriate zinc/lead sulfide scale inhibitor or chelant was added to prevent deposition after the samples were taken. The higher than expected iron concentration in the water was determined to be coming from the reservoir fluids as the downhole completion is Cr<sup>25</sup> and no Cr was found in the produced water. These data are shown in Table 4. The transport pipeline is treated with corrosion inhibitor and there was no evidence of corrosion following direct examination of the pipeline wall thickness.

Though heavy completion fluids were used for these production wells they were not zinc bromide based. The formation of the sulfide scale is believed to arise from the combination of the hydrogen sulfide within the gas phase with the lead and zinc ions within the produced water as the fluid leaves the reservoir at 170°C and cools during processing. The pH of the fluids will rise as the pressure falls and the dissolved carbon dioxide leaves solution - this combined with the decline in temperature probably accounts for the occurrence of more significant scale deposits within the low pressure/colder parts of the system.

The scale control chemical was apparently controlling the formation of carbonate but struggling with sulfate scale in the high salinity brine and in the presence of >200 ppm iron. Dynamic inhibition test work was repeated with and without the presence of 250 ppm of dissolved iron. The dynamic tube blocking test results<sup>18</sup> suggest that the phosphonate scale inhibitor can control carbonate/sulfate scale in the presence of 250 ppm iron much more effectively than some alternative polymer-based scale inhibitors. However, generally, polymer-based scale inhibitors are adversely affected by the presence of such high concentrations of dissolved iron. Based on this test work the scale inhibitor treat rate was increased from 30 ppm to 60 ppm.

While a low molecular weigh phosphonate is controlling sulfate/carbonate scale, it is not controlling the deposition of lead and zinc sulfide scale. At present the low molecular weight acid polymeric inhibitor, which was successfully been trialled on fields B and C (described below) is being deployed in conjunction with the currently used carbonate/sulfate scale control chemical. The chemical treat rate is being optimised based on the levels of lead and zinc ion present within the processed fluids across the separator and hydrocyclone.

**Fields B and C within the Norwegian sector of the North Sea.** Field B was discovered in 1974. It is situated 280 km south west of Stavanger. The reservoir trap is a dip-closed salt dome structure in Upper Jurassic Sandstone - 160 million

years old and located some 3,345 meters below the seabed. The sandstone consists mainly of quartz grains, with additional grains of feldspar and mica and a cement of quartz and calcite. Pressure support for field B's production is enhanced through both water and gas re-injection and some of the production wells require gas lift for continuous production. There are 18 well slots of which 7 are producers, 4 are water injectors and one is a gas injector. The process plant is able to handle 160,000-180,000 bbls of total liquids and 50 MMSCFD of associated gas. The gas-oil ratio is approximately 625 SCF/STB and gas is processed through scrubbers and dehydrators before it reaches the WAG (water-alternating-gas) compressor before injection. Some gas extracted from the first stage separators is used as fuel gas. Production commenced in October 1986 and average oil production in 1998 was 30,458 BOPD at a water cut of approximately 66%. Peak annual production was 126,654 STO barrels per day (1993). The field has recoverable reserves of roughly 435 million barrels of oil, 167 billion cubic feet of gas, and 42.8 million barrels of NGL. The formation water chemistry is presented in Table 5.

Field C was discovered in 1981. It is located 270 km south west of Stavanger and 28 km South East of field B. The reservoir trap is again in Upper Jurassic Sandstone. The reservoir is located between 3,600 and 4,100 meters below the seabed and has a thickness of about 100 meters. The field is now supported by seawater injection. There are 32 well slots of which 12 are for producers with a further 9 wells dedicated to water injection. The first oil was produced in June 1990 and peak annual production was 126,654 STO barrels per day (1993). Recoverable reserves are roughly estimated at 435 million barrels of oil, 167 billion cubic feet of gas, and 42.8 million barrels of NGL. Average oil production in 1998 was 34,056 BOPD at a water cut of approximately 30%. The formation water chemistry is presented in Table 5.

Key process equipment at Field C had been prone to frequent fouling by zinc sulfide scale deposition. Scale removal has been both time, labour intensive and also had associated health risks. At the time the sulfide scale was detected (late 1998), no commercial lead/zinc sulfide inhibitors where available to prevent this type of scale.

Based upon successful operational experience from Field B with a polymer-based scale inhibitor, it was decided to field trial a similar type of chemical at Field C. The principle site of zinc sulfide scale disposition had been the crude oil cooler and the HP-hydrocyclones. Clean-out frequency of these process units had been around every six weeks and was both labour and time consuming. As a result of this, the scale removal in these units had an adverse effect on the other duties which the offshore operators have to fulfil.

Scale removal was carried out using of high strength acids (36% HCl) which both possesses a health risk to the operators

as well as endangering the pipelines and process equipment. A particular hazard when removing zinc sulfide scale with acid is the formation of H<sub>2</sub>S. The predominantly duplex constructed process system was also very sensitive to H<sub>2</sub>S and there is an associated risk of hydrogen cracking. To reduce this risk, H<sub>2</sub>S-scavenger was used to minimize the extent of H<sub>2</sub>S-formation when removing the zinc sulfide scale with hydrochloric acid.

The formation of zinc sulfide scale in the cooler and HP-hydrocyclones had a significant impact on the production and profitability of field C. Scale removal and subsequent bypassing of equipment affected a wide range operational parameters which the operating company employed to measure asset performance. The removal of the sulfide scale was associated with large direct costs. Not only the purchase of acid and H<sub>2</sub>S-scavenger required for the removal but also the seals in the process units were prone to damage during the removal operation and had to be replaced. When the crude oil cooler was bypassed owing to scale formation and subsequent removal from operation, the LP-separator received oil from the HP-separator at very high temperatures (up to 100°C) which caused more flashing of gas in the LP-separator. This resulted in condensate being lost into the gas system. The operation philosophy was to operate the system to minimise loss of oil/condensate to the gas phase. Increased flashing of the gas in the LP-separator represented a direct loss in oil production. When the hydrocyclones were bypassed for clean out there was also a drop in oil in water performance.

A successful intervention against zinc sulfide scale deposition in the oil cooler and HP-hydrocyclones would yield savings in the operational removal cost, both direct and indirect, and help to maximize oil production through cooling of inlet crude prior to the LP-separator. Time would also be freed for both operators and mechanics allowing them to complete their scheduled work. HSE rewards included removing of the health risk to the operators during acid treatments. It was in the interest of both the operator and the Chemical supplier to prevent scale deposition rather than remove the deposits once formed. The solution to this problem was only possible through the development of an integrated scale management team with operation and service company personnel working together to overcome the deposition of this type of scale. Product evaluation was carried out by a field trial of a range of polymeric scale inhibitors that had been short-listed based on their generic type and previous application history.

Field C's production well A-30 had been identified as being a primary contributor to the zinc sulfide scale deposition in Field C's topside equipment. At the time of the trial, it was producing 80-90% of the free zinc ions observed topside (up to 70 ppm Zn<sup>2+</sup>). It was decided to carry out the chemical's scale inhibiting performance evaluation in this well. This required that the well be put on the test-separator for sampling. By injecting the test chemical, which was a low molecular

weight (<10,000 daltons) acid polymer into this well, it was hoped that a marked effect on the residual zinc ion would be seen.

A baseline zinc ion content was established and the differential pressure across the oil cooler between the first and second stage separators was monitored during the trial period. The treat rate was steadily reduced from 50 ppm to 25 ppm based upon water production.

The test chemical effect on the crude oil cooler during the trial period was as follows:-

- Upon start up of the trial, the pressure drop across the cooler was around 2.0 bar. Ordinarily the pressure drop across the unit continued to increase sharply and when the pressure drop reached 3.0 bar, the unit was bypassed for scale removal. However, the pressure drop across the unit went down from 2.0 to 1.4 bar during the course of the trial.
- The performance of the cooler was improved yielding a lower exit crude oil temperature.

From this test, it was evident that the scale inhibitor chemical applied at around 25 to 30 ppm in the water phase had prevented further build up of zinc sulfide and had in fact removed zinc sulfide scale from the crude oil cooler. As the application pH of the chemical solution was pH 5.8, it is not simple acid dissolution of the sulfide scale thus must arise from complexion of the polymer with the zinc ions.

An unexpected benefit of the chemical application was the improvement of the oil-in-water performance. The inhibitor chemical is partly surface active in nature and will position itself at the interface between oil and water in the separators. Depending upon the relationship between the injected volume of test chemical and injected volume of demulsifier, the result may be that the interface in the separators can be tightened. Also the presence of fines such as scale particles within the produced water will stabilise the interface between oil and water so preventing effective separation. If the inhibitor also acts as a dissolver, it will remove the zinc sulfide fines thus improving separation. The overall effect of the polymer treatment at 25 ppm was an improvement in oil-in-water performance and less carryover of water on the oil side of the separator. During the trial, a record value of 5 ppm oil to sea was achieved which is 80 % below the target oil-in-water level set at 26 ppm.

### Conclusions

1. Lead and zinc sulfide scales are extremely insoluble at typical formation brine pH, and salinity. Their solubility increases with increasing brine salinity, temperature and falling pH.
2. The source of lead and zinc ion in many cases is not from heavy completion fluids but from the formation water itself as it reaches thermodynamic equilibrium with

- authigenic or detritial formation minerals such as galena and sphalerite. The source of the sulfide ion is from hydrogen sulfide within reservoir water or gas phases.
3. Lead and zinc sulfide scale occurrence has been reported when high salinity brines are produced along with oil and gas within the Gulf of Mexico, onshore USA, North Sea both UK and Norwegian sector. The formation of such deposits can result in expensive mitigation and significant deferred oil production.
  4. The careful assessment of water chemistry both connate and aquifer is essential prior to field development to allow novel scale types (zinc, lead and iron sulfide) to be assessed and a mitigation strategy developed.
  5. Chemical and physical removal of sulfides, where effective, can only be regarded as shortterm solutions. Chemical dissolution, though relatively effective, does raise issues with corrosion, hydrogen and chloride cracking of metal flowlines/vessels and safety issues related to the handling the hydrogen sulfide that is generated during such a reaction.
  6. Chemical means of inhibition do exist and in this paper examples of such applications have been presented that appear to be able to control the deposition of zinc sulfide scale. One of these products (a low molecular weight polymer) has been used for topside treating, applied via continuous injection upstream of the HP separators.
  7. The developed chemical inhibition system relies on a polymer-based scale inhibitor and can be used in conjunction with the scale inhibitor currently used for sulfate and carbonate control with no adverse interference effects. The polymer chemistry used to control deposition or improve dispersion proved more effective than phosphonate-based scale inhibitors at controlling zinc sulfide scales.
  8. Although the treatment rates do appear to be higher than would be expected for conventional sulfate/carbonate scale inhibitors (25-30 ppm for sulfide where it might only be 2 -5 for the same amount of sulfate scale). The use of scale inhibitor would appear to offer a cost effective alternative method to conventional techniques for the control of zinc and lead sulfide scales.

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Table 1. Scale inhibitors tested in this study for effectiveness against zinc sulfide scale formation.

Abbrev/Name	Type	Composition	GMW
<b>TEAPE</b>	<b>Phosphate Ester</b>	<b>Triethanolamine triphosphate ester</b>	<b>392</b>
<b>DTPMP</b>	<b>Phosphonate</b>	<b>Diethylenetriaminepenta (methylene phosphonic acid)</b>	<b>573</b>
<b>HEDP</b>	<b>Phosphonate</b>	<b>1-Hydroxyethylidene-1, 1-diphosphonic acid</b>	<b>206</b>
<b>ATMP</b>	<b>Phosphonate</b>	<b>Aminotri (methylene phosphonic acid)</b>	<b>299</b>
<b>AMPS/AA</b>	<b>Polymer</b>	<b>AMPS/Sodium acrylate copolymer</b>	<b>2000</b>
<b>PHOS/MA</b>	<b>Polymer</b>	<b>Phosphinated maleic polymer</b>	<b>4000</b>
<b>PAA2</b>	<b>Polymer</b>	<b>Polyacrylic acid</b>	<b>1000</b>
<b>PMA/AMPS</b>	<b>Polymer</b>	<b>Polymaleic/acrylic/AMPS terpolymer</b>	<b>4000</b>
<b>Sequestrene 30A</b>	<b>Chelating Agent</b>	<b>Tetrasodium ethylenediaminetetraacetate</b>	<b>380</b>
<b>CHEL DTPA-41</b>	<b>Chelating Agent</b>	<b>Pentasodium diethylenetriaminepentaacetate</b>	<b>503</b>

Table 2. Field A formation water composition obtained from a drill stem test (DST) on which initial product selection was based and typical fluid composition now that the water cut has risen.

	Initial Water Composition	Production Fluids 29/09/99
Water sample source	DST	Process platform
Depth, feet TVDSS	15,797	-
Reservoir	Pentland	Wells P1, P2
Total dissolved solids	148,930	N/D
SG @ 60°F	1.108	N/D
Resistivity @ 60°F	0.084	N/D
pH @ 60°F	7.53	N/D
Sodium	41,590	29,300
Potassium	345	209
Calcium	11,790	8,875
Magnesium	955	745
Barium	1,690	1,475
Strontium	680	560
Manganese	N/D	N/D
Total iron	8	169
Chloride	91,200	59,491
Sulfate	16	11
Bicarbonate	625	N/D
Carbonate	NIL	N/D
Boron	52	N/D
Silicon	16	N/D
Phosphorus	1.8	N/D
Hydrogen sulfide	20	<30

Table 3. Composition analysis of solid samples recovered from Field A.

Location	HP sep LCV	Location	Flange Deposit	Pig Receiver	HP sep LCV
% Wt Loss on solvent Dried Residue	15.7 84.3	% Wt Loss on ignition Acid insoluble	39.11 48.86	12.05 9.94	16.61 54.71
Chemical analysis of dried residue		Acid soluble			
Fe	41.9	Fe	0.57	51.56	0.81
Mn	0.44	Mn	N/D	N/D	
Zn	9.36	Zn	0.56	1.16	6.93
Pb	4.02	Pb	0.91	1.08	11.31
Ca	0.47	Ca	0.14	0.21	0.02
Ba	3.42	Ba	3.22	0.5	0.02
Na	0.96	Na	N/D	0.64	N/D
SiO <sub>2</sub>	1.83	SiO <sub>2</sub>	N/D	N/D	N/D
SO <sub>4</sub>	2.65	SO <sub>4</sub>	3.42	2.05	6.8
S	5.01	S	N/D	N/D	N/D
		Acid insoluble			
		Ca	0.05	N/D	0.18
		Ba	26.38	N/D	27.53
		Sr	0.15	N/D	0.26
		SO <sub>4</sub>	19.13	N/D	16.16
		SiO <sub>2</sub>	0.62	N/D	0.16
		Fe	0.03	N/D	0.06
Magnetic			Non magnetic	Magnetic	Non magnetic

Table 4. Produced water compositions from water samples taken across the process facilities on the same day of production, Field A. Note: a correction has been made to LP hydrocyclone and LP separator due to the dilution effect that happens in the LP fluid stream.

Date 06/12/99	Location HP Sep	HP Hydrocyclone	LP Hydrocyclone	Dilution Corrected LP Hydrocyclone	LP Separator	Dilution Corrected LP Separator	Degasser
K	ppm 375	ppm 355	ppm 200	ppm 352.8	ppm 200	ppm 359.2	ppm 360
pH	5.1	5.16	5.69	-	5.66	-	5.16
Fe	215	230	135	238.14	130	233.48	225
Ba	2260	2230	1230	2169.7	1210	2173.16	2190
Sr	855	865	500	882	500	898	840
SO <sub>4</sub>	3	< 1	3.5	6.174	2.8	5.0288	3.3
HCO <sub>3</sub>	21	22	31	54.684	31	55.676	22
Cr	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Zn	8.1	8.2	4.6	8.1	4.4	7.9	7.7
Pb	0.09	0.07	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

Table 5. Formation waters and injection water for fields B and C.

Property	Field B (ppm)	Field C (ppm)	Injection Water (ppm)
Na	52555	65340	10890
K	3507	5640	460
Mg	2249	2325	1368
Ca	34675	30185	428
Sr	1157	1085	8
Ba	91	485	0
Cl	153025	167400	19700
SO <sub>4</sub>	44	0	2960
CO <sub>3</sub>	0	0	0
HCO <sub>3</sub>	134	76	124
pH	5.4	5.46	8
Zn	10 – 40	40 – 70	0
Pb	< 1	< 1	0
H <sub>2</sub> S	< 20	20 – 25	0
Res. T	143	150	-
Res. P	410 bar	450 bar	-
WHFT	110	68	-
WHFP	20 bar	25-60	-

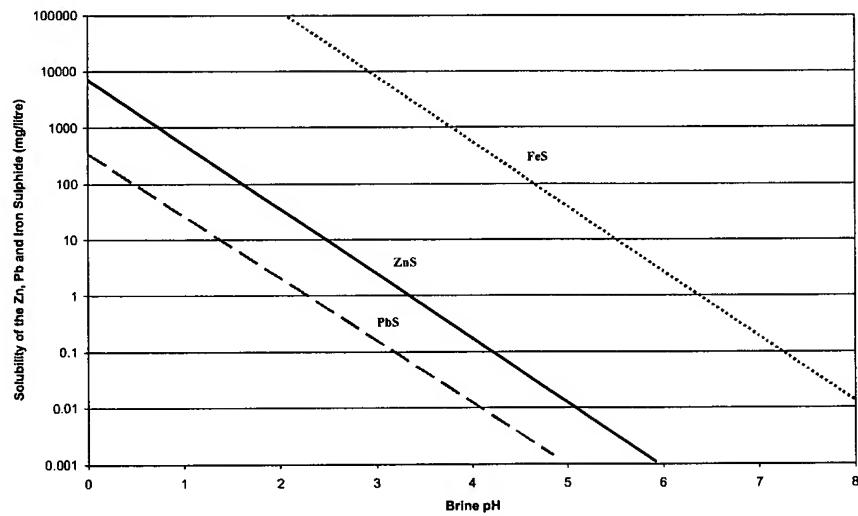


Figure 1. Comparison of zinc, lead and iron sulfide solubility in 1M NaCl brine at 25°C.

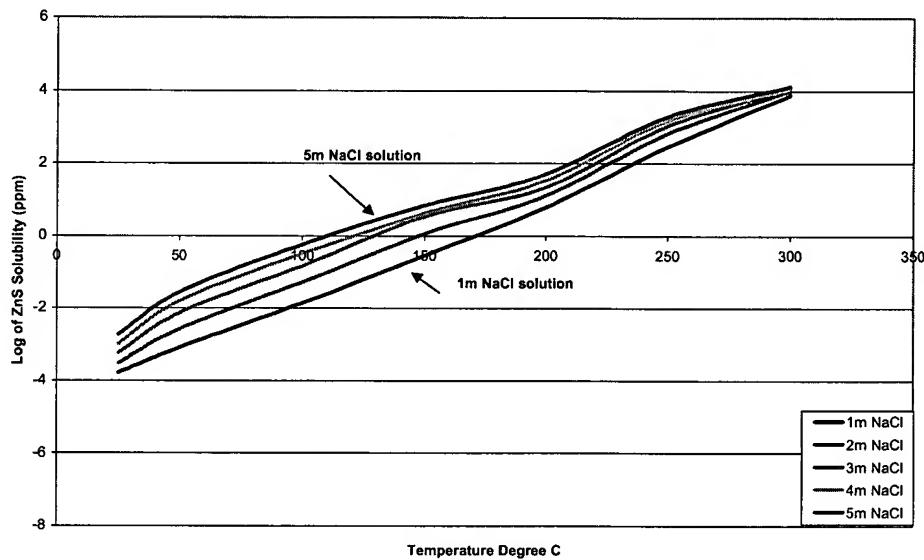


Figure 2. Calculated zinc sulfide solubility at 25°C to 300°C in 1M, 2M, 3M, 4M and 5M NaCl solutions at pH 4.0

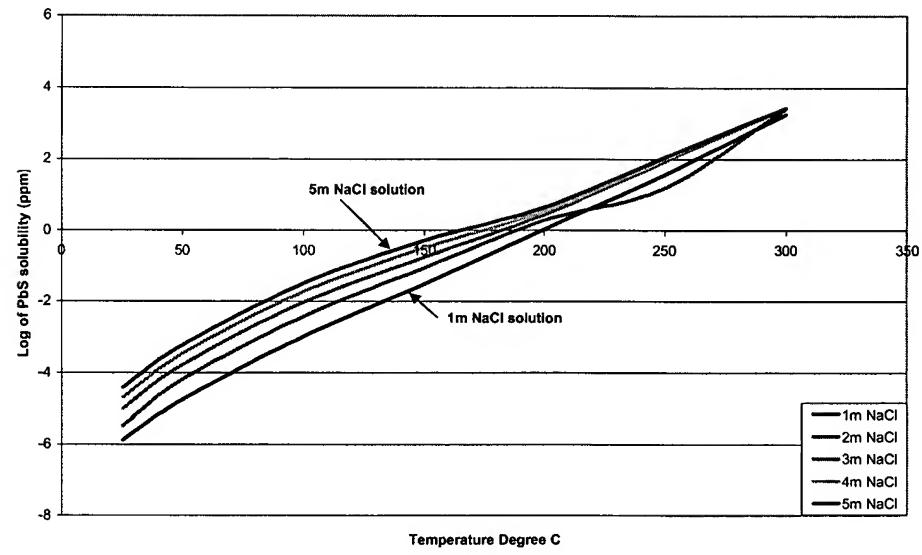


Figure 3. Calculated lead sulfide solubility at 25°C to 300°C in 1M, 2M, 3M, 4M and 5M NaCl solutions at pH 4.0

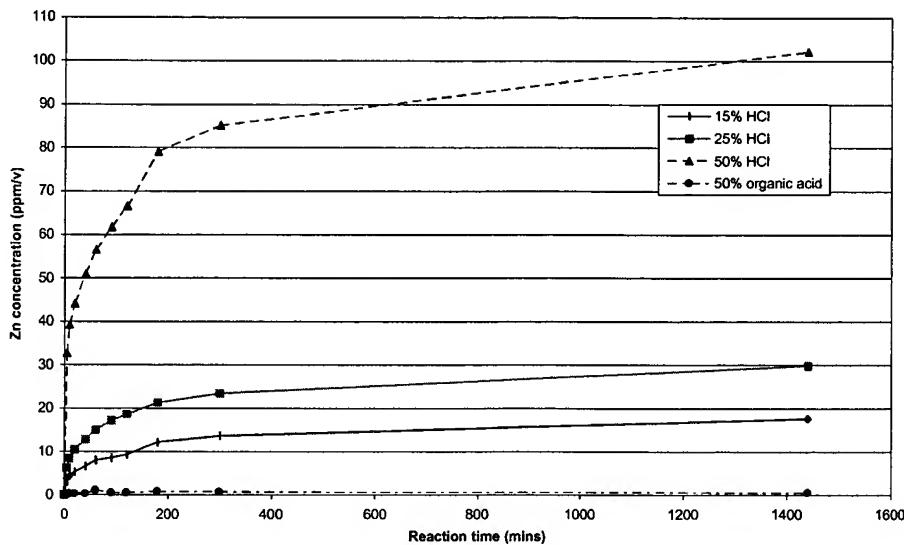


Figure 4. Zinc sulfide scale dissolver performance tests for hydrochloric acid and mixed organic acid at 20°C using 1mm diameter Sphalerite chips

#### Zinc Sulphide Scale Inhibition by a Phosphate Ester Scale Inhibitor

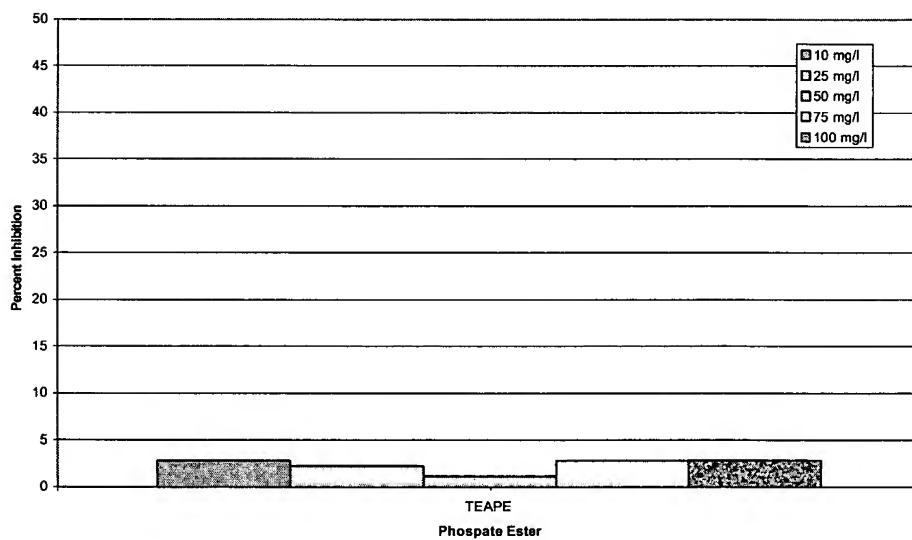


Figure 5. Zinc sulfide inhibition by Phosphonate Ester scale inhibitor

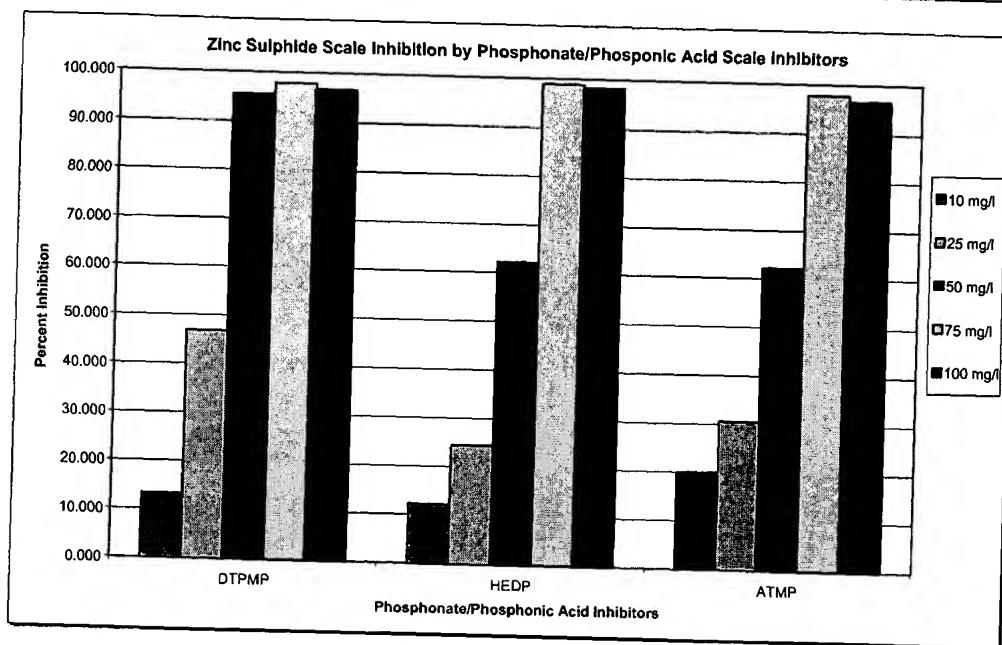


Figure 6. Zinc sulfide inhibition by phosphonate based scale inhibitors

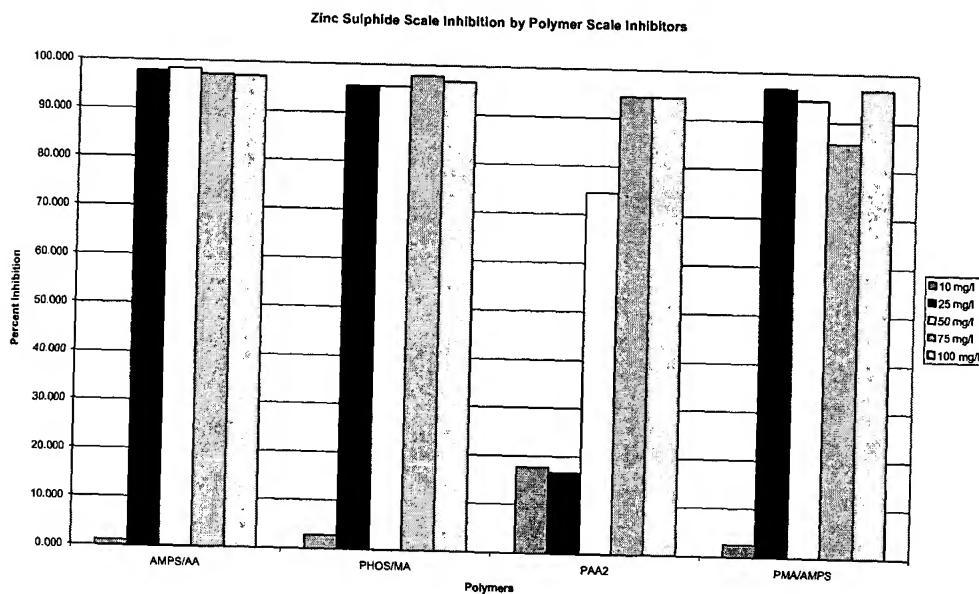


Figure 7. Zinc sulfide inhibition by polymer-based scale inhibitors

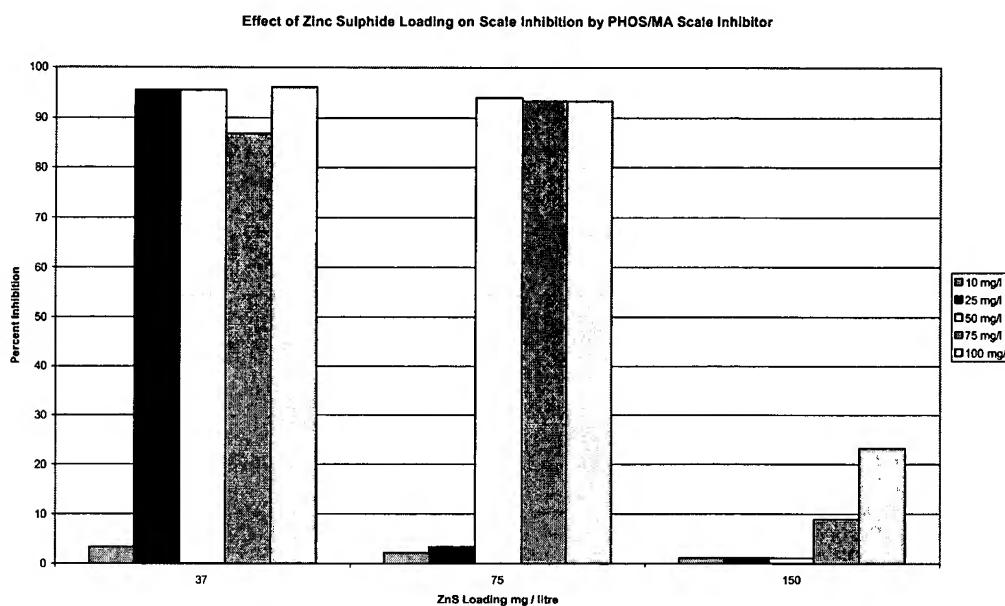


Figure 8. Effect of zinc sulfide concentration on the efficiency of a range of polymer-based scale inhibitors

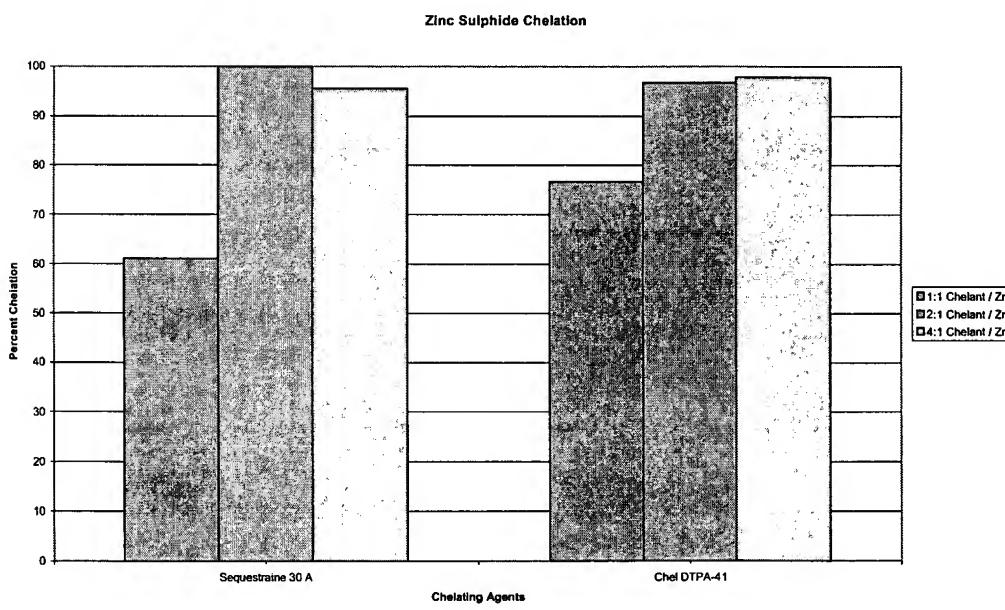


Figure 9. Effectiveness of chelating agents at controlling zinc sulfide deposition.

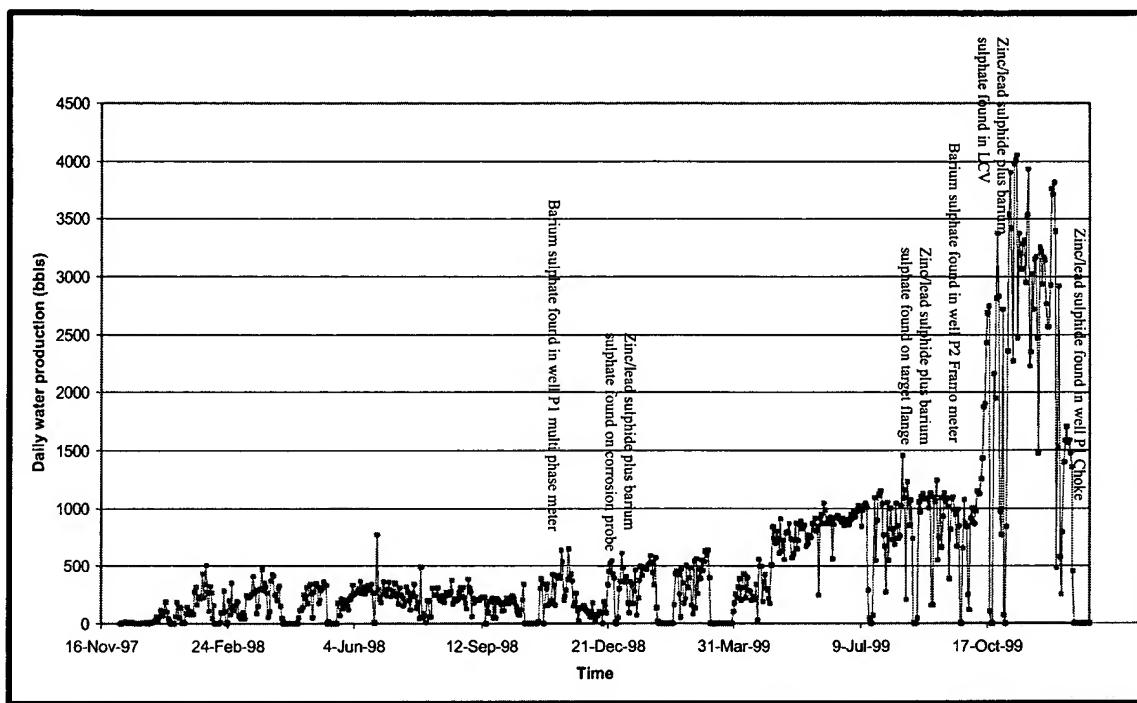


Figure 10. History of scale deposition within field A as water production rates increase. The figure shows the trace amounts of scale observed during the low water production rates which become more significant in amount as water production rates rises sharply in late 1999.